Environmental Mercury Measurement: Fundamentals, History, Experience and Current Status in the USA for Research and Monitoring of Air, Emissions and Field Samples

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Tekran Instruments Research and Development

Symposium on Mercury Pollution Prevention and the International Mercury Convention
Beijing, December 8-9, 2015
How will the Minimata Convention monitor changes in the mercury biogeochemical cycle?

Part pert trillion concentrations – importance of speciation – matrix challenges – Good data needed for fate and effects models

- Wet and Dry Deposition
- Sources

- Lake
- Ocean

Mercury is methylated in waterbodies, then bioaccumulates in fish

Fishing
- commercial (mostly marine)
- recreational (marine/freshwater)
- subsistence (mostly freshwater)

Effects
- Neurological and developmental in children
- Cardiovascular in adults
- Others?

Ecosystem Transport and Transformation

Exposure

Health Impacts
Why did Mercury Measurement and Equipment Improve from 1990 to 2010?

1. Many large government funded research studies in Europe, Canada and the USA

2. Mercury Regulation Development and Implementation

- Will the Minimata Convention drive similar investments and improvements in mercury research and monitoring capabilities?
Four Key Developments for Environmental Mercury Measurement in last 25 Years

1. Adoption of trace-metal clean techniques

2. Application of cold-vapor atomic fluorescence spectrometry (CVAFS) for ultra-trace level measurements

3. Methods were developed for mercury speciation in water, air and flue gas emissions

4. Use of automated, continuous speciation analysis systems providing high resolution characterization of mercury in air and flue gas emissions
Development #1 – Trace Metal Clean Techniques for Mercury

Before 1980 - Inaccurate results due to contamination

After 1980 – Accurate results by using trace-clean sampling, handling and measurements techniques (EPA Method 1669)

Very important to discuss and adopt clean-technique standards within the Minimata mercury monitoring process!
Development #2: Cold Vapor Atomic Fluorescence (CVAF)

Bloom and Fitzgerald (1988) showed the value of the combination of clean techniques with sensitive and reliable Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS).

- Mercury atoms in the cell absorb light energy.
- They re-emit radiation (fluoresce) at the same wavelength.
- Re-emission is omnidirectional.
- Photo detector measures increase in intensity against a dark background.
Development #2: Cold Vapor Atomic Fluorescence (CVAF)

- Ambient Air Gaseous Hg
- Automated and Continuous
- High time resolution
- Typical use in AQM Stations

High Arctic GEM 1995-2005
# Development #3 Trace-Level Mercury Speciation Methods

<table>
<thead>
<tr>
<th>Method / Regulation</th>
<th>Matrix</th>
<th>Equipment Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>USEPA Method 1631E</td>
<td>Water, Sediments, Biota, Rainwater</td>
<td>CVAFS – Tekran 2600-IVS</td>
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<tr>
<td>Total Mercury</td>
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<td></td>
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<tr>
<td>USEPA Method 1630</td>
<td>Water, Sediments, Biota, Rainwater</td>
<td>CVAFS – Tekran 2700</td>
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<tr>
<td>Methy-Hg, Ethyl-Hg</td>
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<tr>
<td>USEPA 15852:2008</td>
<td>Ambient Air</td>
<td>CVAFS Tekran 2537X</td>
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<tr>
<td>Total Gaseous Mercury</td>
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<td>EN 15852:2008</td>
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<tr>
<td>AMNets, GMOS</td>
<td>Ambient Air</td>
<td>CVAFS Tekran 2537-1130-1135</td>
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<td>Speciated Mercury</td>
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<tr>
<td>USEPA MATS and PC-MACT</td>
<td>Flue Gas Emissions</td>
<td>CVAFS Tekran 3300Xi</td>
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Development #3 Example:
Mercury Speciation in Water and Biota

EPA Method 1630
Automated Analysis
All Organo-Hg Species
DEVELOPMENT #4
USE OF AUTOMATED, CONTINUOUS SYSTEMS FOR AMBIENT AIR

GEM = Gaseous Elemental Mercury
GOM = Gaseous Oxidized Mercury
PBM = Particulate Bound Mercury
How hard can it be to measure air mercury fractions?

- Difficult matrix
- Minimize surface reactions or losses during transport
- Short sample times to maximize species integrity
- Must separate and collect GOM and PBM without capturing any GEM

**GOM & PBM ~ 1 ppqv**

**GEM ~ 170 ppqv**

Calvert and Lindberg (2005)
Question: What is the best method for atmospheric mercury fractionation?

- **Criteria:** Continuously measure GEM, PBM\(_{2.5}\) and GOM with hourly resolution and DL<5 pg/m\(^3\) (0.5 ppqv) for trends, source-receptor models and impacts of reduced emissions due to regulations.

- **USEPA Initiative and Scientific Consensus:** was to use a 2.5 um inlet > annular denuder > particulate filter > gold-trap CVAFS
USEPA Designed Automated Hg Fractionation Method

Method is:
- Lab tested
- Widely published
- QA Challenged
- Used by all networks
- Designed for research work

- Quartz wool filter
- PBM
- GOM
- KCl-coated annular denuder
- 2.5 um Inlet
- Automated Gold-trap CVAFS
Automated Mercury Fractionation Method using Tekran 2537-1130-1135 Equipment

Some reasons why the current AMNet
Automated Mercury Speciation System is nearly ideal:

- Uses a known and accepted method to separate large particles, fine particles and gases
- Depends on laminar flow and minimizing potential surface losses (impactor > annular denuder > filter)
- Has the capability for the user to control sampling temperature of all collection and transport surfaces
- Annular denuder may be customized with different coatings. KCl has worked well in most cases, but other coatings may work better
- Short sample time and near-time analysis to maximize sample integrity and refresh the collection surface, with a blank reported for each sample run
- Critical – Total mercury accuracy is robust, so mass balance and data coherence evaluation is possible
- Highly resolution GEM, PBM, and GOM data are useful for modelers/urban transport models
Example Air Mercury Fractionation Data at USA Rural Site Near Emission Sources
Air Measurement Networks using Tekran Equipment

CANADA Research and Monitoring Sites
Air Measurement Networks using Tekran Equipment

AMNET – USA * CANADA * ASIA
Air Measurement Networks using Tekran Equipment

CHINA - Research and Monitoring Sites
Air Measurement Networks using Tekran Equipment

EUROPE - Research and Monitoring Sites
Air Measurement Networks using Tekran Equipment

GMOS - Global Mercury Observation System
DEVELOPMENT #4

USE OF AUTOMATED, CONTINUOUS SYSTEMS FOR FLUE GAS
U.S. EPA EGU MATS and Cement MACT
Summary – [Hg] must be really low ~ 1.5 ug/m³ for EGUs

- **EPA Electric Generating Unit**
  Mercury and Air Toxic Standards (MATS) promulgated January 2012

- **Targeted MATS Pollutants and limits**

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<tr>
<th>Pollutant</th>
<th>Existing Source Std.</th>
<th>New Source Std.</th>
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<tbody>
<tr>
<td>Mercury</td>
<td>1.2 lbs/T BTU</td>
<td>0.35 lbs/T BTU</td>
</tr>
<tr>
<td>PM</td>
<td>0.03 lbs/M-BTU</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>0.002 lbs/M BTU</td>
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- **The EPA Portland Cement MACT**
- **Targeted MACT Pollutants and limits**

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<td>Mercury</td>
<td>55 lbs/MM tons clinker</td>
<td>21 lbs/MM tons clinker</td>
</tr>
<tr>
<td>THC</td>
<td>24 ppmvd</td>
<td>24 ppmvd</td>
</tr>
<tr>
<td>PM</td>
<td>0.07 lbs/ton clinker</td>
<td>0.02 lbs/ton clinker</td>
</tr>
<tr>
<td>HCl</td>
<td>3 ppmvd</td>
<td>3 ppmvd</td>
</tr>
<tr>
<td>Organic HAP (Alternative to THC)</td>
<td>12 ppmvd</td>
<td>12 ppmvd</td>
</tr>
</tbody>
</table>

**Deadline for Compliance – April, 2015**

**Deadline for Compliance – September, 2015**
The coal flue gas **matrix** is very challenging

**Conversion** of Hg$^{2+}$ to Hg$^{0}$ quantitatively with long-term robustness is critical for success

Quantitative **transport** of Hg species from probe to detector requires:

- Dilution with dry air
- High temperatures for Hg$^{2+}$ - no cold spots
- Inert surface materials
**MATRIX:** Accurately Measuring pptv* Levels of Mercury in Coal Flue Gas

- 1 µg/m3 Hg = 112 parts per trillion (v/v)
- Accurate measurements requires understanding and managing the many potential mercury redox reactions with halogens, sulfur oxides and water in the gas phase and on surfaces
- Tekran R&D spent 1998 to 2003 understanding flue gas mercury reactions in the laboratory
- Detectors can only measure Hg⁰
CONVERSION: The Challenge of Mercury and Reactive Halogens

- Hg$^0$ + reactive halogen is our friend and foe:
  - Required for Hg analysis by HgCEMs and direct thermal method for sorbent traps (30B)
  - Helpful for Hg control and used for HgCEM performance checks

- Bi-directional reaction affected by
  - Temperature
  - Catalytic surface reactions
  - Gas and particle matrix

**Bi-directional reactions**

For analysis, Hg$^0$ formation must be quantitative with no back reaction

\[ \text{HgCl}_2 \leftrightarrow \text{Hg}^0 + \text{Cl}_2 \]

For control, HgX$_2$ formation and capture needs to be quantitative with no back reaction to minimize release of Hg$^0$

\[ \text{Hg}^0 + \text{Br}_2 \leftrightarrow \text{HgBr}_2 \]

*Simplified chemistry for illustration purposes only*
Tekran 3300Xi HgCEM Flue Gas Converter/Conditioner (patented)

- Task: quantitatively convert all Hg$^{2+}$ to Hg$^0$ with no back reactions in a complex flue gas matrix
- Proprietary thermal converter material set at 700 degrees C
- DI water injected into tail of thermal converter to “fix” Hg$^0$ from potential back reactions and eliminate interferences
- Gas is rapidly chilled, water condenses and removes reactive compounds. Only Hg$^0$ remains in clean gas matrix for analyzer
EERC Study Low-Level Measurements
(funded by EPRI, ICCI, CATM in 2010)

One example of many independent field trials done in the USA
Mercury Speciation in Flue Gas

Speciation data in flue gas provides knowledge about control choices and down wind impacts using models.

![Graph showing speciation data in flue gas](graph.png)

- Total Hg
- Hg^0
- Hg^{2+}
Cabinet-Based Tekran 3300Xi HgCEMS
Configuration for Regulatory Monitoring

Interior 3300Xi HgCEMS Cabinet

Cabinet for HgCEMS
Tekran 3300Xi Dual Port Sampling

Applications:

- Mercury control technology evaluation
- Regulatory monitoring of multiple emissions stacks.
Tekran 3300RS (Research Systems)

3300RS-Dual Probe

3300RS Upstream Injection
U. of Ningbo-Nottingham Hg Control Technology Configuration with 3300-RS

Slide courtesy of Professor Tao Wu’s Research Lab at the U. of Nottingham-Ningbo
Example data from Johnson Matthey
Conversion of Hg$^0$ to Hg$^{2+}$ across a catalyst

Simulated flue gas
Good Total Hg Mass Balance at inlet/outlet
Shows Hg$^0$ to Hg$^{2+}$ conversion across a catalyst

Slide courtesy of Michael Nash at Johnson Matthey
Research Groups Using Tekran 3300 Systems

- **China** — Univ. Nottingham-Ningbo, Jiaotong U., Zhejiang U., Huaneng Clean Energy Institute, Guodian Longyuan, Guodian Nanjing, Huazhong U.

- **USA** — USEPA, Cormatech, Gore, Ablemarle, Coalogix, EERC

- **England** — Johnson Matthey

- **Poland** — CCTW Zabzre
Conclusions

- Require the use of trace metal clean techniques!
- For China – the sooner air, deposition, water and biota monitoring programs begin, the more value they will have as emissions are reduced.
- More government investment needed to improve current measurement methods and technology and to develop new mercury sensors.